

JP 5-32746
2/9/93vs. PD
7/2/93

1-14 ep act
polycarb
P-19 solder
resist
P-22 partial epox

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P-14
(M)AA: epoxy
0.8:1.5:1

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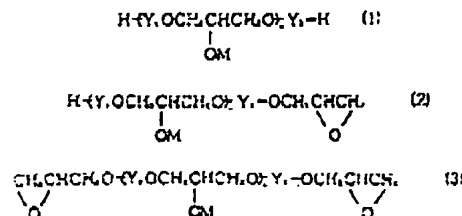
(54) [Title of the invention] Resin compositions, solder resist resin compositions and cured materials made from the same

(57) [Abstract] (to be amended)

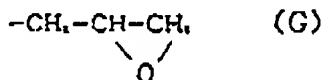
[Objectives] To provide a resin composition useful as a solder resist resin composition capable of providing a cured material having excellent adhesion capability, electrical insulation capability, solder heat resistance, gold plating resistance and chemical resistance as well as a cured material made from the same.

[Aspect] A resin compositions and a solder resist resin composition comprising an unsaturated group-containing polycarboxylic acid resin which is a reaction product between the reaction product of an epoxy resin having a structure represented by Formula (1), (2) or (3) with (meth)acrylic acid

and a polybasic carboxylic acid or its anhydride as well as a cured material made from the same.



wherein each of Y_1 and Y_2 denotes independently an aromatic residue, n is an integer of 1 or more, and M denotes a hydrogen atom or a group represented by Formula (G):

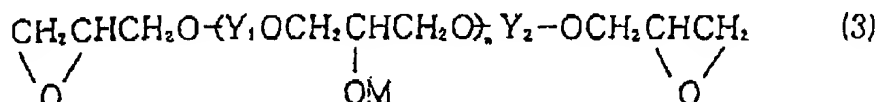
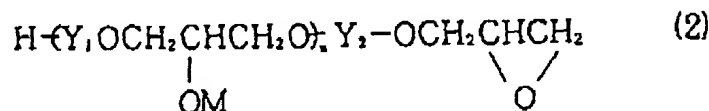
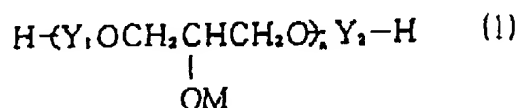


provided that when n is 1 then M is represented by Formula (G) and when n is 2 or more then at least one M is represented by Formula (G).

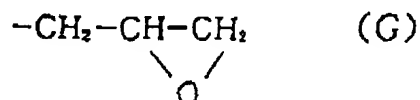
[What is claimed is:]

[Claim 1] A resin compositions comprising an unsaturated group-containing polycarboxylic acid resin which is a reaction product between the reaction product of an epoxy resin having a structure represented by Formula (1), (2) or (3):

(Formula (1), (2), (3))



wherein each of Y_1 and Y_2 denotes independently an aromatic residue, n is an integer of 1 or more, and M denotes a hydrogen atom or a group represented by Formula (G):



provided that when n is 1 then M is represented by Formula (G) and when n is 2 or more then at least one M is represented by Formula (G) with (meth)acrylic acid and a polybasic carboxylic acid or its anhydride.

[Claim 2] A solder resist resin composition comprising an unsaturated group-containing polycarboxylic acid resin according to Claim 1.

[Claim 3] A cured material made from a resin composition according to Claim 1 or 2.

[Detailed description of the invention]

[Field of the invention] The present invention relates to a resin composition having an excellent developability and capable of providing a cured film having excellent adhesion

capability, solder heat resistance, chemical resistance, gold plating resistance and electrical insulation capability, which contains an unsaturated group-containing polycarboxylic acid resin and which is useful as a solder resist resin composition for a printed circuit board, as well as a cured material made from the same.

[Prior art] Recently, an increased number of UV-curable compositions were employed in various fields because of the reasons such as resource saving, energy saving, improvement in handling and higher producibility. Also in the field of printed circuit board processing, various inks such as solder resist inks and marking inks employ more and more UV-curable compositions instead of conventional thermosetting compositions because of the reasons mentioned above. Among these, the solder resist inks have first employed the UV-curable compositions.

[Problems to be solved by the invention] While screen printings have been employed as resist pattern forming methods for printed circuit boards, such screen printings involve problems such as bleeding, blurring and running of the inks observed frequently during the printing process, because of which they can not be applied to current highly integrated printed circuits.

In order to solve these problems, photoresists of a dry film types and liquid developable resist inks were proposed and

employed, but a photoresist of such dry film type also involves disadvantage that it readily undergoes blistering upon heat compression, has poorly reliable heat resistance and adhesion capability, and is expensive. On the other hand, commercially available liquid resists include those employing organic solvents as developers and those developed with dilute aqueous solutions of alkalis, but those employing organic solvents involve problems such as air pollution, expensive solvents and insufficient solvent and acid resistances of cured material.

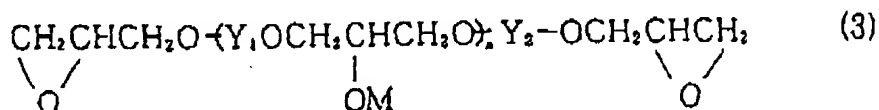
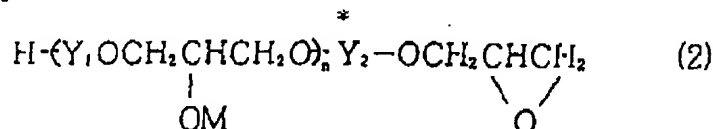
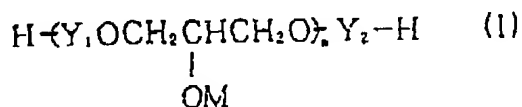
Those developable with dilute aqueous solutions of alkalis also involve disadvantageous characteristics such as whitening of the surface of a cured resist after solder heat resistance test in an aqueous flux system and the gold plating resistance is not sufficient.

[Means to solve the problems] We made much effort to solve the problems mentioned above and was finally successful in providing a resin composition useful as a solder resist resin composition which can be developed with an aqueous solution of an alkali and can provide a cured film having excellent adhesion capability, solder heat resistance, chemical resistance and goldplating resistance, and whose surface does not become white after solder heat resistance test in an aqueous flux system, as well as a cured material made from the same.

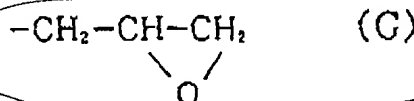
Accordingly, the present invention relates to:

- 1) a resin compositions comprising an unsaturated group-

containing polycarboxylic acid resin which is a reaction product between the reaction product of an epoxy resin having a structure represented by Formula (1), (2) or (3):



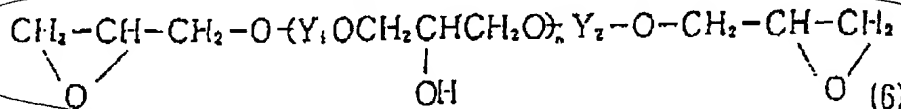
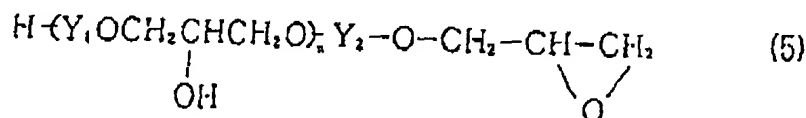
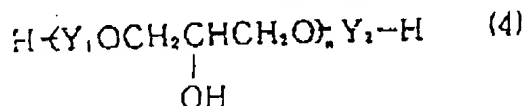
wherein each of Y_1 and Y_2 denotes independently an aromatic residue, n is an integer of 1 or more, preferably 1 to 2, and M denotes a hydrogen atom or a group represented by Formula (G):



provided that when n is 1 then M is represented by Formula (G) and when n is 2 or more then at least one M is represented by Formula (G) with (meth)acrylic acid [acrylic acid, methacrylic acid or a mixture thereof] and a polybasic carboxylic acid or its anhydride;

- 2) a solder resist resin composition comprising an unsaturated group-containing polycarboxylic acid resin according to 1) indicated above; and,
- 3) a cured material made from a resin composition according to 1) or 2) indicated above.

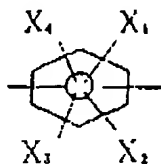
An epoxy resin represented by Formula (1), (2) or (3) can be obtained by reacting the alcoholic hydroxyl group of a composition represented by Formula (4), (5) and (6):



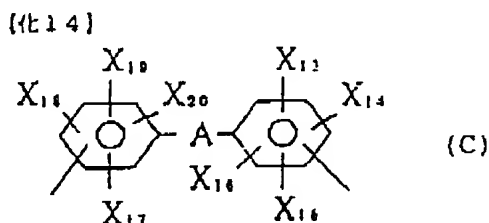
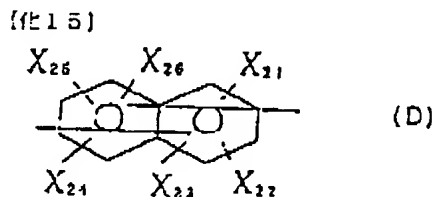
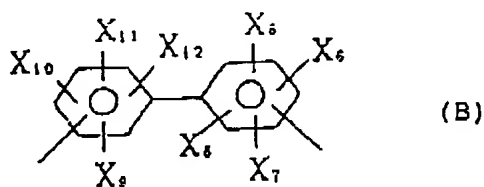
wherein each of Y_1 and Y_2 denotes independently an aromatic residue and n is an integer of 1 or more, with an epihalohydrin such as epichlorohydrin preferably in the presence of dimethylsulfoxide.

Y_1 and Y_2 in Formula (1), (2), (3), (4), (5) or (6) denote the aromatic residues such as, for example, those represented by formulae:

(Formula A, B, C, D (Chemical Structure No.12 to 15))

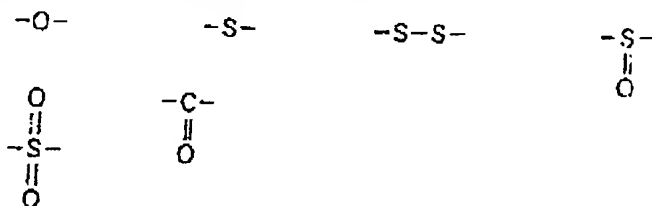


(A)



wherein A denotes an alkylene; a cycloalkylene; an alkylene substituted with alkyl, perfluoroalkyl, cycloalkyl or aryl group; a group represented by formulae:

(Chemical Structure No.16);



or a group represented by formula:

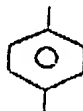
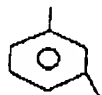
(Chemical Structure No.17),



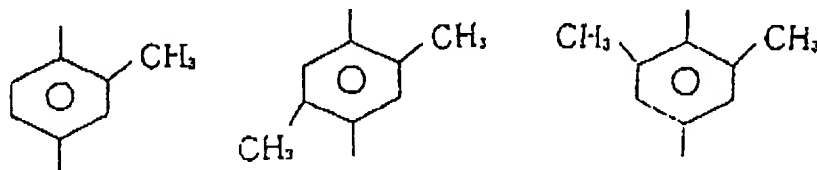
and each of X_1 to X_{26} denotes independently a hydrogen atom, an alkyl group or a halogen group. The group represented by Formula A includes, for example, those represented by formulae:

(Chemical Structure No.18 to 23)

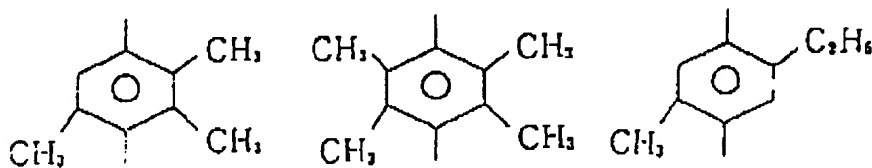
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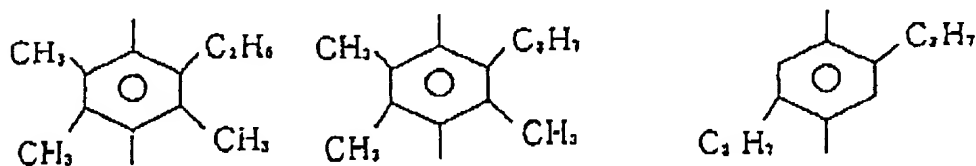
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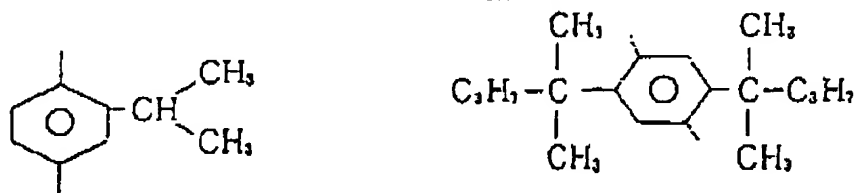
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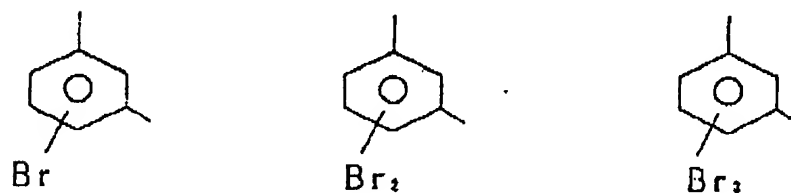
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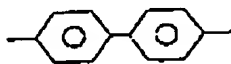
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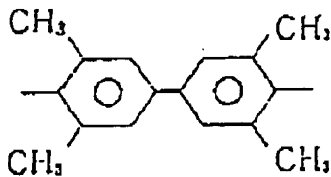
the group represented by Formula B includes, for example, those represented by formulae:

(Chemical Structure No.24 to 25)

(化24)



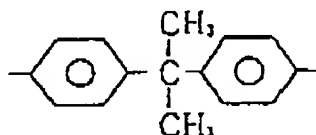
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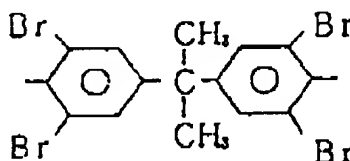
the group represented by Formula C includes, for example, those represented by formulae:

(Chemical Structure No.26 to 45)

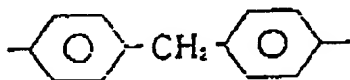
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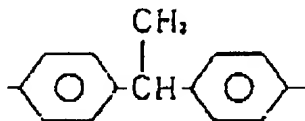
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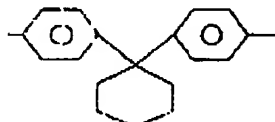
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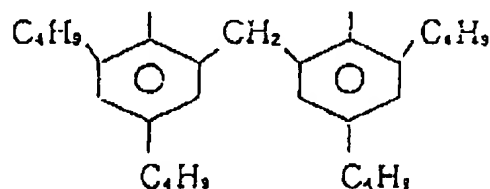
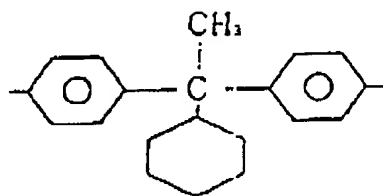
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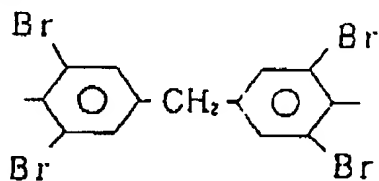
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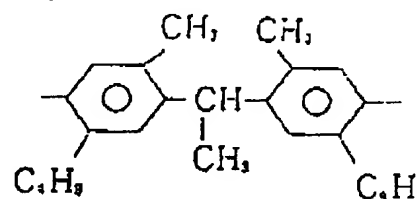
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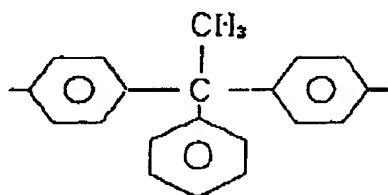
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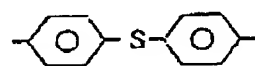
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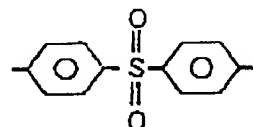
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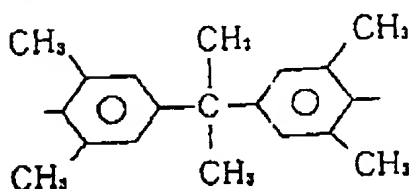
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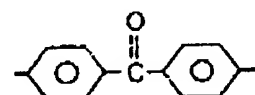
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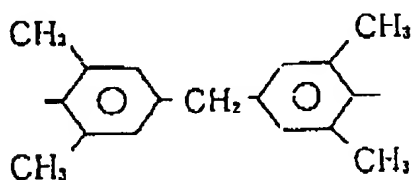
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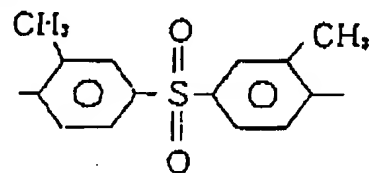
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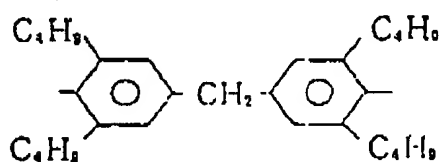
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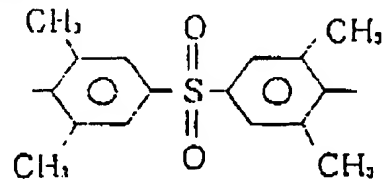


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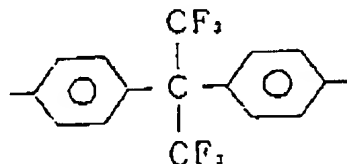
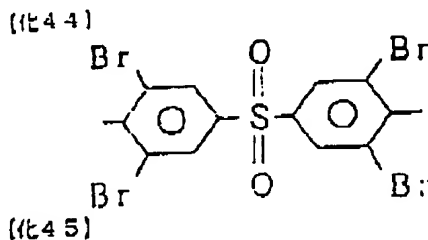


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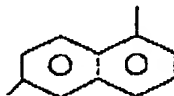
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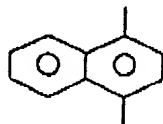
and, the group represented by Formula D includes, for example, those represented by formulae:

(Chemical Structure No. 46 to 47)

(46)



(47)



The amount of an epihalohydrin may be 1 equivalent or more per 1 equivalent of the alcholic hydroxyl group in Formula (4), (5) or (6). An amount exceeding 15 equivalents or more per 1 equivalent of the alcholic hydroxyl group results in no advantage corresponding to the increase in the amount and affects the volume efficiency adversely.

When dimethylsulfoxide is employed, it may preferably be used in an amount of 5 to 300 % by weight based on a compound represented by Formula (4), (5) or (6). An amount less than 5 % by weight based on a compound represented by Formula (4),

(5) or (6) results in a prolonged reaction time due to the slow reaction between the alcoholic hydroxyl group in Formula (4), (5) or (6) and an epihalohydrin, while an amount exceeding 300 % by weight based on a compound represented by Formula (4), (5) or (6) results in almost no effect of the increase in the amount as well as a poor volume efficiency.

When conducting the reaction, an alkali metal hydroxide is employed. Such alkali metal hydroxide includes sodium hydroxide, potassium hydroxide, lithium hydroxide and calcium hydroxide with sodium hydroxide being preferred. The amount of an alkali metal hydroxide employed may be almost 1 equivalent per 1 equivalent of the alcoholic hydroxyl group in Formula (4), (5) or (6) which is intended to be epoxidized. Also an excess amount may be used when all of the alcoholic hydroxyl group in a compound represented by Formula (4), (5) or (6), an amount exceeding 2 equivalents per 1 equivalent of the alcoholic hydroxyl group may results in a slight polymerization.

An alkali metal hydroxide may be employed as a solid or as an aqueous solution. When used as an aqueous solution, the reaction may be conducted with distilling the water in the reaction system off under atmospheric or reduced pressure into the outside of the reaction system. The reaction temperature is preferably 30 to 100°C. A reaction temperature below 30°C results in a slow reaction, which requires a prolonged reaction time. A reaction temperature exceeding 100°C results in an

undesirable side reaction.

After completion of the reaction followed by distilling excessive epihalohydrin and dimethylsulfoxide off under reduced pressure, a product resin may be dissolved in an organic solvent and subjected to dehalogenation hydrogenation with an alkali metal hydroxide. On the other hand, after completion of the reaction, the reaction mixture may be washed with water to separate a by-product salt and dimethylsulfoxide, and excessive epihalohydrin in the organic phase is distilled off from under reduced pressure, and then the resin is dissolved in an organic solvent and subjected to dehalogenation hydrogenation with an alkali metal hydroxide. Such organic solvent includes methylisobutylketone, benzene, toluene and xylene, with methylisobutylketone being preferred. The solvents may be employed independently or as a mixture with others.

An unsaturated group-containing polycarboxylic acid resin may be obtained by reacting the reaction product between an epoxy resin produced by the method mentioned above and (meth)acrylic acid (epoxy(meth)acrylate) with a polybasic carboxylic acid or its anhydride.

The reaction between an epoxy resin and (meth)acrylic acid may be conducted in the ratio of about 0.8 to 1.5 equivalent of (meth)acrylic acid per 1 equivalent of the epoxy group in the epoxy resin.

A diluent employed preferably during the reaction includes solvents such as methylethylketone, ethyl cellosolve acetate, butyl cellosolve acetate, carbitol acetate, diethylene glycol dimethylether and solvent naphtha, and reactive monomers such as carbitol (meth)acrylate, phenoxyethyl (meth)acrylate, pentaerythritol tetra(meth)acrylate, trimethylol propane tri(meth)acrylate, tris(hydroxyethyl) isocyanurate tri(meth)acrylate, dipentaerythritol hexa(meth)acrylate, polypentaerythritol poly(met)acrylate and the like.

In addition, it is preferable to use a catalyst (for example, triethylamine, benzylmethylaniline, methyltriethyl ammonium chloride, triphenylstibine) for promoting the reaction, and the amount of a catalyst employed is preferably 0.01 to 10 % by weight, more preferably 0.3 to 5 % by weight based on the mixture of starting materials.

In order to prevent polymerization during the reaction, it is preferable to use a polymerization inhibitor (for example, methoquinone, hydroquinone, phenothiazine) preferably in an amount of 0.01 to 1 % by weight, more preferably 0.05 to 0.5 % by weight based on the mixture of starting materials. The reaction temperature is preferably 60 to 150°C, more preferably 80 to 120°C. The reaction time is preferably 5 to 60 hours, more preferably 10 to 50 hours.

An unsaturated group-containing polycarboxylic acid

resin can be obtained by reacting epoxy (meth)acrylate described above with a polybasic carboxylic acid or its anhydride (for example, maleic acid, phthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, HEAD acid and anhydrides of these acids) (esterification reaction of the hydroxyl group in epoxy (meth)acrylate). The reaction described above is conducted preferably by reacting an acid or its anhydride mentioned above in an amount of 0.05 to 1.00 equivalents per 1 equivalent of the hydroxyl group with epoxy (meth)acrylate. The reaction temperature is 60 to 150°C, preferably 80 to 100°C.

The acid value of an unsaturated group-containing polycarboxylic acid resin (mgKOH/g) is preferably 30 to 150, more preferably 50 to 120. The amount of an unsaturated group-containing polycarboxylic acid resin contained in a composition according to the present invention is preferably 10 to 90 % by weight, more preferably 20 to 80 % by weight, based on the composition.

A composition according to the present invention may additionally contain epoxy resins such as phenol novolac epoxy resins, cresol novolac epoxy resins, bisphenol epoxy resins and tris (2,3-epoxypropyl)isocyanurate, as well as the reaction products between these epoxy compounds and (meth)acrylic acid, i.e., epoxy (meth)acrylates and/or reactive monomers described above. The amount employed is preferably 0 to 100 parts by

weight per 100 parts by weight of an unsaturated group-containing polycarboxylic acid resin.

When an epoxy compound listed above is employed, one or more epoxy resin hardener (for example, dicyanedi- amide and its derivatives, imidazol compounds, triazine compounds, urea compounds, aromatic amines, polyphenol compounds and cationic photopolymerization catalysts) may be employed. When an epoxy resin hardener is employed, the amount added is preferably 0.5 to 50 parts by weight per 100 parts by weight of an epoxy compound described above.

Although electron beam, ultraviolet or heat may be employed for curing a composition according to the present invention to obtain a cured material, curing with ultraviolet followed by heat if necessary is preferred. When ultraviolet is employed for curing, a photopolymerization initiator is used. Although such photopolymerization initiator may be any of conventional known photopolymerization initiator, one having satisfactory storage stability after incorporation is preferred.

Such photopolymerization initiator includes, for example, benzoine, benzyl, benzoisomethylether, benzoine isopropylether, acetophenone, 2,2-dimethoxy-2-phenylacetophenone, 2,2-diethoxy-2-phenylacetophenone, 1,1-dichloroacetophenone, 1-hydroxycyclohexyl phenylketone, 2-methyl-2-[4-(methylthio)phenyl]-2-morpholinopropan-1-one,

N,N-dimethylaminoacetophenone, 2-methylanthraquinone, 2-ethylanthraquinone, 2-t-butylanthraquinone, 1-chloroanthraquinone, 2-amylanthraquinone, 2-aminoanthraquinone, 2,4-dimethylchioxanthone, 2,4-diethylthioxanthone, 2,4-diisopropylthioxanthone, acetophenone dimethylketal, benzophenone, methylbenzophenone, 4,4'-dichlorobenzophenone, 4,4'-bisdiethylaminobenzophenone, Michler's ketone and the like. These compounds may be employed independently or in combination.

Such photopolymerization initiator may also be combined with one or more known customary photosensitizers such as ethyl N,N-dimethylaminobenzoate, isoamyl N,N-dimethylaminobenzoate, triethanolamine, triethylamine and the like. A preferable combination is 2,4-diethylthioxanthone or 2-isopropylthioxanthone with ethyl N,N-dimethylaminobenzoate, 2-methyl-2-[4-(methylthio)phenyl]-2-morpholinopropan-1-on (Ciba-Geigy, IRGACURE 907) with 2,4-diethylthioxanthone or 2-isopropylthioxanthone.

The amount of a photopolymerization initiator employed is preferably 0 to 50 parts by weight, more preferably 4 to 35 parts by weight per 100 parts by weight of an unsaturated group-containing polycarboxylic acid resin.

A composition according to the present invention may further contain inorganic fillers such as talc, silica, alumina, barium sulfate and magnesium oxide and coloring pigments such

as cyanine green and cyanine blue. Melamine resins such as hexamethoxymelamine, hexabutoxymelamine, thixotropy agent such as aerosil, levelling agents such as silicone, fluorine polymers, acrylic copolymers, antifoam agents, UV absorbers, antioxidants, polymerization inhibitors may also be incorporated if necessary.

A composition according to the present invention can be obtained by incorporating the ingredients in the ratio described above and mixing uniformly using a roll mill and the like. A composition of the present invention can be cured to obtain a cured material according to a standard method described below. Thus, it is cured with ultraviolet light and further with heat if necessary to obtain a cured material. When heat is used for curing, the heating temperature is preferably 20 to 170°C, and the heating period is preferably 30 minutes to 2 hours.

When a composition of the present invention is employed as a solder resist resin composition, it may be cured as described below to obtain a cured material. Thus, a composition according to the present invention is applied at a film thickness of 10 to 100 μ m onto a printed circuit board by means of screen printing, spraying, roll coating, static application or curtain flow coating method, and the film is dried at 60 to 80°C and then brought into direct contact with a negative film, to which ultraviolet light is then irradiated, and subsequently

the non-irradiated region of the film is dissolved off using an aqueous solution of an alkali, such as a 0.5 to 2 % aqueous solution of sodium carbonate, a 0.5 to 1 % aqueous solution of sodium hydroxide or an aqueous solution of potassium hydroxide, and then the film is cured by heating at 120 to 170°C for a period of 30 minutes to 1 hour to obtain a cured film.

While a composition according to the present invention is useful as a solder resist resin composition, it may also be employed as an insulating paint, a printing ink, an adhesive and a coating. A resin composition comprising an unsaturated group-containing polycarboxylic acid resin according to the present invention is excellent in terms of developability, hardness of a cured material, solder heat resistance, acid resistance, alkali resistance, gold plating resistance etc., and causes less whitening of the surface after solder heat resistance test in an aqueous flux system.

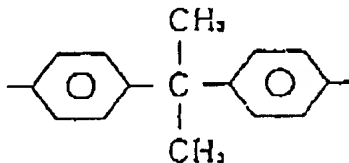
[Examples] The present invention is further illustrated in Examples described below. In Synthesis and Examples, the parts are the parts by weight.

(Synthesis of epoxy resin)

(Synthesis 1) 371 Parts of a bisphenol A epoxy resin (epoxy resin (f)) whose Y_1 and Y_2 in Formula (6) were both represented by the group:

(Chemical structure 4B)

p. 7
bisphenol A-
advanced
DGEBA



and which had the mean n of 3.3, the epoxy equivalent of 650, the hydrolyzable salt content (% by weight of the chlorine atom contained in the compound, quantified by titrating the chloride ion, which has been liberated by dissolving the epoxy resin in dioxane followed by addition of 1N alcoholic solution of potassium hydroxide followed by heating under reflux for 30 minutes, with silver nitrate) of 0.39%, the softening point of 81.1°C and the melting viscosity (150°C) of 12.5 poise was dissolved in 925 parts of epichlorohydrin and 462.5 parts of dimethylsulfoxide, and 52.8 g of 98.5% NaOH was added with stirring over 100 minutes at 70°C.

After addition, the reaction was continued at 70°C for further 3 hours. Then most of the excessive unreacted epichlorohydrin and dimethylsulfoxide were distilled off under reduced pressure and the reaction product containing a by-product salt and dimethylsulfoxide was dissolved in 750 g of methylisobutylketone and reacted for further 1 hour at 70°C in the presence of 10 g of 30 % NaOH.

After completion of the reaction, the mixture was washed twice with 200 g of water. After phase separation, the organic phase was evaporated to remove methylisobutylketone to yield 340 g of epoxy resin (a) having the epoxy equivalent of 287, the hydrolyzable chlorine content of 0.07 %, the softening point

of 64.2°C and the melting viscosity (150°C) of 7.1 poise. In
2 epoxy resin (a) thus obtained, about 3.1 out of 3.3 alcoholic
3 hydroxyl groups in Formula (6) were epoxidized based on the
calculation from the epoxy equivalent.

Synthesis 2

The reaction was conducted similarly as in Synthesis 1
except for using 24.3 g of 98.5 % NaOH to yield 365 g of epoxy
resin (b) having the epoxy equivalent of 379, the hydrolyzable
chlorine content of 0.067 %, the softening point of 76.8°C and
the melting viscosity (150°C) of 11.1 poise. In epoxy resin
11 (b) thus obtained, about 1.7 out of 3.3 alcoholic hydroxyl
12 groups in Formula (6) were epoxidized based on the calculation
from the epoxy equivalent.

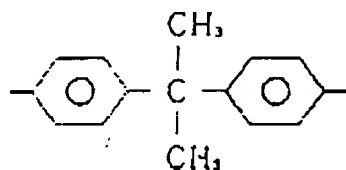
Synthesis 3

The reaction was conducted similarly as in Synthesis 1
except for using 13.3 g of 98.5 % NaOH to yield 350 g of epoxy
resin (c) having the epoxy equivalent of 444, the hydrolyzable
chlorine content of 0.054 %, the softening point of 79.5°C and
the melting viscosity (150°C) of 11.5 poise. In epoxy resin
20 (c) thus obtained, about 1.0 out of 3.3 alcoholic hydroxyl
21 groups in Formula (6) were epoxidized based on the calculation
from the epoxy equivalent.

Synthesis 4

Except for using 442 g of epoxy resin (epoxy resin (g))
whose Y₁ and Y₂ in Formula (6) were both represented by the group:

(Chemical structure 49)

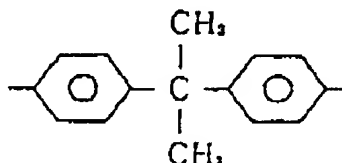


and which had the mean n of 2.2, the epoxy equivalent of 483, the hydrolyzable salt content of 0.097 %, the softening point of 67.0°C and the melting viscosity (150°C) of 3.4 poise instead of epoxy resin (f), the reaction was conducted similarly as in Synthesis 1 to yield 450 g of epoxy resin (d) having the epoxy equivalent of 274, the hydrolyzable chlorine content of 0.03 %, the softening point of 56.1°C and the melting viscosity (150°C) of 2.7 poise. In epoxy resin (d) thus obtained, about 1.9 out of 2.2 alcoholic hydroxyl groups in Formula (6) were epoxidized based on the calculation from the epoxy equivalent.

Synthesis 5

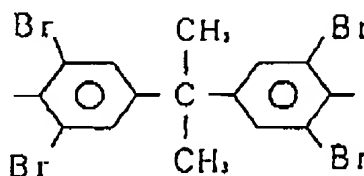
Except for using 641 g of a low-bromine type epoxy resin (epoxy resin (h)) whose Y₁ and Y₂ in Formula (6) were represented by the group:

(Chemical structure 50)



and by the group:

(Chemical structure 51)



respectively, and which had the mean n in Formula (6) of 1.5, the epoxy equivalent of 493, the hydrolyzable salt content of 0.106 %, the softening point of 70.7°C, the melting viscosity of 4.1 poise and the bromine content of 21.1 % instead of epoxy resin (f), the reaction was conducted similarly as in Synthesis 1 to yield 631 g of epoxy resin (e) having the epoxy equivalent of 304, the hydrolyzable chlorine content of 0.052 %, the softening point of 57.8°C, the melting viscosity (150°C) of 1.9 poise and the bromine content of 19.4 %. In epoxy resin (e) thus obtained, almost all of 1.5 alcoholic hydroxyl groups in Formula (6) were epoxidized based on the calculation from the epoxy equivalent.

(Synthesis of unsaturated group-containing polycarboxylic acid resin)

Synthesis 6

287 g Parts of epoxy resin (a) obtained in Synthesis 1, 68.5 parts of acrylic acid, 0.5 parts of methoquinone, 2.0 parts of triphenylphosphine and 191.4 parts of carbitol acetate were charged and heated to 95°C, at which the reaction was conducted until the acid value of the reaction mixture (mgKOH/g) became 1.0 or less (about 35 hours), and then the mixture was cooled to 60°C, and subsequently 101.3 parts of tetrahydrophthalic anhydride and 54.5 parts of carbitol acetate were charged and the mixture was heated to 90°C, and the reaction was conducted until the acid value (solid acid value excluding solvent,

mgKOH/g) became 71 to obtain an unsaturated group-containing polycarboxylic acid resin (product A). The viscosity of product A (25°C, poise) was 310 poise.

Synthesis 7

379 g Parts of epoxy resin (b) obtained in Synthesis 2, 68.5 parts of acrylic acid, 0.7 parts of methoquinone, 2.5 parts of triphenylphosphine and 241 parts of carbitol acetate were charged and heated to 95°C, at which the reaction was conducted until the acid value of the reaction mixture (mgKOH/g) became 1.0 or less (about 35 hours), and then the mixture was cooled to 60°C, and subsequently 99 parts of maleic anhydride and 53.3 parts of carbitol acetate were charged and the mixture was heated to 90°C, and the reaction was conducted until the acid value (solid acid value excluding solvent) became 100 to obtain an unsaturated group-containing polycarboxylic acid resin (product B). The viscosity of product B (25°C, poise) was 395 poise.

Synthesis 8

444 g Parts of epoxy resin (c) obtained in Synthesis 3, 68.5 parts of acrylic acid, 0.8 parts of methoquinone, 2.8 parts of triphenylphosphine and 276 parts of carbitol acetate were charged and heated to 95°C, at which the reaction was conducted until the acid value of the reaction mixture (mgKOH/g) became 1.0 or less (about 35 hours), and then the mixture was cooled to 60°C, and subsequently 133 parts of phthalic anhydride and

71.6 parts of carbitol acetate were charged and the mixture was heated to 90°C, and the reaction was conducted until the acid value (solid acid value excluding solvent) became 78 to obtain an unsaturated group-containing polycarboxylic acid resin (product C). The viscosity of product C (25°C, poise) was 450 poise.

Synthesis 9

483 g Parts of epoxy resin (d) obtained in Synthesis 4, 81.8 parts of methacrylic acid, 0.9 parts of methoquinone, 3.1 parts of triphenylphosphine and 304 parts of carbitol acetate were charged and heated to 95°C, at which the reaction was conducted until the acid value of the reaction mixture (mgKOH/g) became 1.0 or less (about 35 hours), and then the mixture was cooled to 60°C, and subsequently 146 parts of hexahydrophthalic anhydride and 78.6 parts of carbitol acetate were charged and the mixture was heated to 90°C, and the reaction was conducted until the acid value (solid acid value excluding solvent) became 75 to obtain an unsaturated group-containing polycarboxylic acid resin (product D). The viscosity of product D (25°C, poise) was 200 poise.

Synthesis 10

493 g Parts of epoxy resin (e) obtained in Synthesis 5, 68.5 parts of acrylic acid, 0.9 parts of methoquinone, 3.1 parts of triphenylphosphine and 302 parts of carbitol acetate were charged and heated to 95°C, at which the reaction was conducted

until the acid value of the reaction mixture (mgKOH/g) became 1.0 or less (about 35 hours), and then the mixture was cooled to 60°C, and subsequently 129.2 parts of tetrahydrophthalic anhydride and 69.6 parts of carbitol acetate were charged and the mixture was heated to 90°C, and the reaction was conducted until the acid value (solid acid value excluding solvent) became 69 to obtain an unsaturated group-containing polycarboxylic acid resin (product E). The viscosity of product E (25°C, poise) was 250 poise.

Example 1 to 5, Comparative 1, 2

According to the composition shown in Table 1 (values represented as % by weight), a solder resist resin composition (ink) was formulated and kneaded using a 3-roll mill. The composition thus obtained was coated onto the entire surface of a copper throughhole printed circuit board to a film thickness after drying of 15 to 25 μm , and the film was pre-dried at 70°C for 15 minutes, and subsequently the back surface was coated similarly and pre-dried at 70°C for 25 minutes.

Then the solder mask pattern film was brought into contact with the coated film surface, and exposed using a metal halide lamp both side simultaneous exposure device (OAK, HMW 680) at the dose of 500 mJ/cm^2 , and then non-irradiated region of the film was developed with 1.0 wt % aqueous solution of sodium carbonate for 60 seconds at the spray pressure of 2.5 kg/cm^2 and at the liquid temperature of 25°C, whereby effecting removal

by solubilization. The printed article thus obtained was evaluated as described below (in terms of developability).

Subsequently, the article was subjected to thermosetting in an oven drier at 150°C for 60 minutes and the test piece having the cured film was evaluated as described below in terms of cured film hardness, solder heat resistance, anti-whitening capability, acid resistance, alkali resistance, solvent resistance, gold plating resistance and insulation resistance. The results are shown in Table 2.

The methods for testing and evaluating are as described below.

(Developability) Developability was evaluated visually using a magnifying glass.

O - Complete development.

Δ - Partly pale and non-developed region.

x - Mostly non-developed region.

(Hardness of cured film) The hardness of a cured film was determined according to JIS K5400.

(Solder heat resistance) According to the method under JIC 6481, a test piece was immersed 10 or 4 times in a solder bath at 260°C each for 10 minutes and the change in appearance was evaluated.

(Postflux resistance) The change in appearance was evaluated after immersing a test piece 10 times each for 10 minutes.

O - No change in appearance.

Δ - Change in color of cured film.

x - Cured film which is released or peeled off or goes under solder.

NOTE) Postflux employed: JS-64P (manufactured by SANEI KAGAKU)

(Resistance against flux for leveller) The change in appearance was evaluated after immersing a test piece 4 times each for 10 minutes.

O - No change in appearance.

Δ - Change in color of cured film.

x - Cured film which is released or peeled off or goes under solder.

NOTE) Postflux employed: SSF-832 (manufactured by SANEI KAGAKU (KK))

(Anti-whitening capability) A flux (LONCO CF-430, manufactured by YOSHIKAWA CHEMICAL (KK)) was applied onto a cured film, immersed in a solder bath at 260°C for 5 minutes followed by hot water at 100°C for 30 minutes, and then the change in appearance was evaluated.

O - No change in appearance.

Δ - Slight whitening.

x - Whitening of entire surface.

(Acid resistance) A test piece was immersed in 10 vol % aqueous solution of sulfuric acid at 25°C for 15 minutes and then the change in appearance was evaluated visually. Adhesion capability was evaluated by subjecting the solder pattern

region to the peeling test using a cellophane adhesive tape and then observing the release of the resist.

O - No change in appearance with no release of cured film.

Δ - No change in appearance with slight peeling of cured film.

x - Release of cured film with marked peeling observed in peeling test.

(Alkali resistance) A test piece was immersed in 10 wt % aqueous solution of sodium hydroxide at 25°C for 15 minutes and subjected to the evaluation similar for the acid resistance.

(Solvent resistance) A test piece was immersed in dichloromethane at 25°C for 30 minutes and the change in appearance was observed.

O - Completely no change in appearance

Δ - Swelling and permeation

(gold plating resistance) After conducting gold plating for 30 minutes at the current density of 1A/dm² using AUTOLONEX Cl (plating liquid) manufactured by CELLEX, the film was subjected to the peeling test using a cellophane tape. The evaluation was based on the following criteria.

O - No peeling.

Δ - Very slight peeling.

x - Peeling of entire surface.

(Insulation resistance) A test piece was examined for its initial insulation resistance and then for the resistance after moisture intake and electric corrosion over 7 days according

to the method under IPC-SM-840B (IPC Class III).

(1) Table 1 (1) (2) Example, (3) Product A, (4) Carbitol acetate, (5) IRGACURE 907, (6) Epoxy resin hardener, (7) Phthalocyanine green (pigment), (8) KS-603 (antifoam agent), (9) Hexamethoxymelamine, (10) Talc

(1) Table 1 (2), (2) Product A, (3) Carbitol acetate, (4) IRGACURE 907, (5) Epoxy resin hardener, (6) Phthalocyanine green (pigment), (7) KS-603 (antifoam agent), (8) Hexamethoxymelamine, (9) Talc, (10) Comparative,

NOTE:

*1 KAYARAD R-5027: Manufactured by NIPPON KAYAKU (KK), Reaction product between a phenol novolac type epoxy acrylate and a dibasic acid anhydride, containing 40 % by weight of butylcellosolve acetate, Acid value: 68.5 (mmKOH/g)

*2 KAYARAD R-5089: Manufactured by NIPPON KAYAKU (KK), Reaction product between a bisphenol A type epoxy acrylate and a dibasic acid anhydride, containing 40 % by weight of carbitol acetate, Acid value: 63 (mmKOH/g)

*3 KAYARAD R-2058: Manufactured by NIPPON KAYAKU (KK), A phenol novolac type epoxy acrylate, containing 30 % by weight of butylcellosolve acetate

*4 TEPIC-S: Manufactured by NISSAN KAGAKU (KK), Tris(2,3-epoxypropyl)isocyanurate, Melting point: 95 to 125°C

*5 EPPN-201: Manufactured by NIPPON KAYAKU (KK), A phenol novolac type epoxy resin, softening point: 65°C

*6 KAYARAD DPHA: Manufactured by NIPPON KAYAKU (KK),
Dipentaerythritol, polyacrylate

*7 IRGACURE 907: Manufactured by Ciba-Geigy,
Photopolymerization initiator

*8 KAYACURE DETX: Manufactured by NIPPON KAYAKU (KK),
Photopolymerization initiator

*9 Dicyanediarnide

*10 2-Ethyl-4-methylimidazol

*11 KS-603: Manufactured by SHINETSU KAGAKU KOGYO (KK),
Antifoam agent

(1)Table 2, (2)Example, (3)Comparative, (4)Developability,
(5)Cured film hardness, (6)Solder heat resistance, (7)Postflux
resistance, (8)Resistance against flux for leveller,
(9)Anti-whitening capability, (10)Acid resistance, (11)Alkali
resistance, (12)Solvent resistance, (13)gold plating
resistance, (14)Insulation resistance, (15)Initial, (16)After
test

Based on the results of the evaluation as indicated in
Table 2, it was evident that the cured material made from an
inventive resin composition was excellent in terms of hardness,
anti-whitening capability, acid resistance, alkali resistance,
solvent resistance and gold plating resistance.

[Effect of the invention] A resin composition according
to the present invention, when used in forming a solder resist
pattern by selective exposure to ultraviolet light through a

pattern-printed film followed by developing unexposed region, exhibits resistance of the exposed region against the developing solution and provides a cured material which is excellent in terms of adhesion capability, electrical insulation capability, solder heat resistance, gold plating resistance and chemical resistance, thus being used suitably as a solder resist resin composition.

) Continued from the front page: Identification number, In-office serial number, Technology disclosure section